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Residential Wood Combustion Study

Task 1
Ambient Air Quality Impact Analysis

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This document describes the project design, methodology and results of the RWC impact monitoring program. The findings of this task form the basis for projections of future RWC impacts discussed under task 2A (~~EPA 910/9-82-089c~~) of this series. They also provide the first comprehensive survey of RWC impacts within Pacific Northwest communities during a period likely to be typical of maximum RWC emissions. Appendices from this task are contained in Report ~~No. EPA 910/9-82-089b~~.

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RESIDENTIAL WOOD COMBUSTION STUDY

TASK 1

AMBIENT AIR QUALITY IMPACT ANALYSIS

RESIDENTIAL WOOD COMBUSTION STUDY

TASK 1

Ambient Air Quality Impact Analysis

FINAL REPORT

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THEY ARE LISTED BELOW FOR YOUR CONVENIENCE.

EPA 910/9-82-089a	Residential Wood Combustion Study Task 1 - Ambient Air Quality Impact Analysis
EPA 910/9-82-089b	Task 1 - Appendices
EPA 910/9-82-089c	Task 2A - Current & Projected Air Quality Impacts
EPA 910/9-82-089d	Task 2B - Household Information Survey
EPA 910/9-82-089e	Task 3 - Wood Fuel Use Projection
EPA 910/9-82-089f	Task 4 - Technical Analysis of Wood Stoves
EPA 910/9-82-089g	Task 5 - Emissions Testing of Wood Stoves Volumes 1 & 2
EPA 910/9-82-089h	Task 5 - Emissions Testing of Wood Stoves Volumes 3 & 4 (Appendices)
EPA 910/9-82-089i	Task 6 - Control Strategy Analysis
EPA 910/9-82-089j	Task 7 - Indoor Air Quality

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ABSTRACT

A Study of Residential Wood Combustion
Task 1: Ambient Air Quality Impact Analysis

The ambient air quality impact of Residential Wood Combustion (RWC) emissions in eight Pacific Northwest cities was studied during the 1980-81 space heating season. Seventy-seven worst case fine particle ambient samples collected in Seattle, Spokane, Yakima, Tacoma and Longview, Washington; Boise, Idaho; Portland and Medford, Oregon were selected and analyzed for Polynuclear Aromatic Hydrocarbon compounds, 35 trace elements and carbon. The impact of RWC and other sources was determined by Chemical Mass Balance calculation and validated against independent carbon-14 measurements.

This document describes the project design, methodology and results of the RWC impact monitoring program. The findings of this task form the basis for projections of future RWC impacts discussed under task 2A of this series. They also provide the first comprehensive survey of RWC impacts within Pacific Northwest communities during a period likely to be typical of maximum RWC emissions.

EXECUTIVE SUMMARY

Recent increases in the use of wood as a source of residential space heating within Pacific Northwest states has led to concerns focusing on public health risks and degrading air quality within many communities. A comprehensive survey of eight cities in Oregon, Washington and Idaho was conducted during the October, 1980 - March, 1981 space heating seasons to provide a better assessment of current maximum 24 hour RWC impacts on particulate air quality. Seventy-seven selected fine particle samples from Seattle, Spokane, Tacoma, Longview and Yakima, Washington; Boise, Idaho; Portland and Medford, Oregon were analyzed for 35 trace elements, carbon, PNA compounds and carbon-14. RWC impacts were then quantified by Chemical Mass Balance and validated by independent carbon-14 measurements.

Source apportionment results typically assign from 66% to 84% of the fine particle mass (less than 2.5 um) and 36-60% of the TSP mass measured in residential land use areas to RWC emissions during selected, worst case woodsmoke conditions. Twenty-four hour, worst cast impacts exceeding 60 $\mu g/m^3$ were measured at residential sites in Seattle, Spokane, Portland, Medford and Boise. A maximum impact of 128 $\mu g/m^3$ (upper limit estimate) was recorded at the Boise residential site. Benzo(a)pyrene concentrations as high as 22 ng/m^3--a factor of ten higher than background--were measured in Spokane.

Results from the ambient monitoring program clearly document the importance of RWC emissions as the most important contributor to fine particle mass concentrations in many Northwest communities during worst case winter particulate air quality conditions.

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1.0 INTRODUCTION

The increasing use of wood (and coal) as a source of residential heat is a phenomenon common to many states in the Pacific Northwest. For a variety of economic and political reasons, the public's interest in the use of wood as an important heating fuel has led to a resurgence in concerns focusing on wood smoke visibility reduction, odors, public health risks and the "livability" of many communities.

The use of wood for residential heating, while aesthetically pleasing, carries a significant potential for adverse health effects to large segments of the population. The impact of Residential Wood Combustion (RWC) emissions is especially severe because plume impacts typically occur at ground level very near to the source. In addition, the areas of highest RWC emission density often coincide with the areas of maximum population density and the majority of the RWC particulate emissions are within the size range deposited within the lungs. RWC emissions are relatively rich in carcinogenic organics, toxic pollutants and respiratory irritants. For all of these reasons, wood smoke represents an important problem that is of growing public concern.

The chemical products formed in the combustion of wood have recently been shown to contain 17 priority pollutants, 14 carcinogenic compounds and 6 toxic or mucus coagulating agents which, when considered in addition to toxic gaseous emissions and respiratory irritants, collectively represent an important health risk.[1]

RWC emissions are becoming increasingly important as a major contributor to violations of current particulate air quality standards and are implicated in issues related to visibility reduction, odors and public health. New attention being focused on the adoption of an Inhalable Particulate National Ambient Air Quality Standard has also caused concern about the RWC impact on 24 hour standard attainment. The continuing economic pressures to expand the use of wood and coal for residential heating, and the limited regulatory pressures restricting the use of wood, may cause additional concern about the impact of RWC emissions on public health, aesthetics and the future "livability" of many communities.

A multi-faceted study of current and projected air quality impacts, fuel use

trends, the current status of wood stove emission testing, RWC control strategy alternatives and indoor exposure has been conducted in response to the current concern over the RWC problem. This document reports on Task 1 in this series; the air quality impact of RWC emissions on ambient air quality. This report focuses on the impact of particulate emissions, although carbon monoxide, aldehydes, phenols, volatile organic compounds and oxide of nitrogen emissions are also of potential concern.

The objective of Task 1 was to estimate the maximum 24 hour impact of RWC emissions in Portland, Oregon, Seattle and Spokane, Washington during the 1980-81 heating season. Historical samples collected in Longview and Yakima, Washington, Boise, Idaho and Medford, Oregon were included to provide a broad-based study representative of Pacific Northwest communities. Other objectives of the program were to (a) determine the ambient concentration of polynuclear aromatic hydrocarbons (PNA) compounds associated with RWC emissions (b) validate RWC impacts calculated by Chemical Mass Balance methods with estimates obtained by Carbon-14 measurements and (c) develop a data base upon which future projections of RWC impacts can be based given fuel use trend information.

2.0 PROGRAM METHODOLOGY

The program design of the RWC Ambient Impact Analysis includes six elements, each of which are important to the program success. Data analysis methods focusing on the Chemical Mass Balance (CMB) model and Carbon-14 techniques, the air sampling program, sample selection, analytical protocol, source characterization and data interpretation methods. Each are described in this section.

2.1 Air Sampling Program

The RWC air sampling program was established and operated to define the ambient particulate impact of residential wood heating emissions in three Northwest cities; Portland, Oregon, Spokane and Seattle, Washington. Sampling was conducted at rural, residential, commercial and industrial land use areas listed in Table 1. The sampling network can be subdivided into two groups:

Table 1

RWC Ambient Sampling Network

Site #	City	Location	Land Use/ Site Type	Sampling Period (1981)	Number of Samples	Monitoring Instrumentation HV	SSI	Sierra	Dichot	Other
1	Spokane	Country Homes	Residential [1]	1/31-3/10	15	x		x	x	
2	Spokane	Turnbull	Background	10/30/80-3/1/81	5	x		x	x	
3	Seattle	Newport Way	Residential	2/6-3/8	10	x		x	x	
4	Seattle	Lake Samamish	Background	3/9/81	1			x	x	
5	Portland	Marcus Whitman School	Residential	1/30-3/5	8	x		x	x	
6	Portland	Carus	Background	2/6-3/5	6	x		x	x	
7	Medford	County Courthouse*	Commercial	12/17/80- 1/16/81	1	x		x	x	
8	Seattle	South Park (Dallas)*	Residential	1/15-1/16	2	x			x	x [2]
9	Tacoma	Fire Station 12*	Industrial	1/4-2/9	4	x			x	x [3]
10	Seattle	Georgetown*	Industrial	10/18/80-2/3/81	3	x			x	
11	Yakima	County Courthouse*	Commercial	11/17/80-2/21/81	4	x			x	x [3]
12	Longview	City Shops*	Commercial	12/11/80-1/16/81	4	x			x	
13	Spokane	County Health*	Commercial	10/31/80	1				x	
14	Spokane	Crown Zellerbach* [1]	Industrial	1/17-3/11	4	x			x	
15	Boise	Fairview & Liberty St.*	Commercial +	12/9/80-2/23/81	9	x	x		x	

Notes:

1. Located about 1 mile from an Aluminum Reduction Plant
2. Cyclone Sampler ($\leq$ 1 μm)
3. Integrating Nephalometer

* Historical Samples

\+ Located in near proximity to Residential development

Sites 1-6 active during the October, 1980 to March, 1981 period and sites 7-15 from which historical samples were selected.

Sites active during the 1980-81 heating season were operated either on a daily or every other day schedule on a 24-hour basis. All residential sites were selected on the basis of the apparent level of wood burning activity as indicated by visible plumes, wood stove stacks and firewood storage piles. Final siting was contingent upon availability of power, security considerations, sampler exposure and adherence to established siting criteria (40 CRF Part 58). Characteristics of specific sites are noted in Appendix 1.

Sampling was planned to concentrate on weekends, when greater use of wood stoves and fireplaces was assumed likely to occur. Flexibility was, however, provided to sample continuously during any air stagnation episodes with cold temperatures. Sampling was planned for the Friday-Monday period, plus a mid-week day, provided weather conditions were sufficiently cold and stable. Weather forecasts were monitored and sampling decisions were made on a daily basis. The following criteria were adopted as guidelines in determining whether or not sampling would be conducted:

1. Predicted minimum temperature of less than 40°F and preferably less than 35°F
2. Daily average wind speeds less than 5 mph
3. Presence of atmospheric inversions

Background site samples were not planned to correspond to each sample collected at each residential site. Instead, 3-6 background samples were selected to represent a range of background levels. Most background site samples did correspond to a residential site sample, however, providing a number of days for each city for which CMB analysis can include comparison of simultaneous in-town and background samples.

Sampling Protocol

The air sampling protocol was intended to capture particulate samples (TSP, respirable and inhalable) for subsequent chemical analysis, to estimate residential wood combustion (RWC) impacts. At each residential and background site, the following instruments were operated for this study:

1. A standard high volume sampler, to measure total suspended particulate (TSP), on glass fiber filter media (hi-vol).
2. A standard high volume sampler equipped with a Sierra Model 235 High Volume Cascade Impactor to collect "respirable" (< 2 microns in particle diameter) aerosols on glass fiber filters (Sierra).
3. A dicholomous sampler to collect a "respirable" or fine fraction (<2.5 μm) and a coarse (2.5-15 μm) fraction on teflon filters.
4. A size selective inlet sampler designed to collect inhalable particles less than 15 μm on glass fiber filters was used at the Boise site (SSI).

Although samplers from EPA Region X, the Oregon Department of Environmental Quality and NEA, INC. were used in the network, most of the sampling instrumentation required was already in regular use at the background monitoring sites in the Portland area (at Carus) and Spokane area (at Turnbull), as part of the regular particulate monitoring network operated by DEQ and the Spokane County Air Pollution Control Agency (SCAPCA), respectively. A new background site was established temporarily in the Seattle area for this study. The dichotomous sampler deployed there was provided by the State of Washington Department of Ecology (DOE) Laboratories.

Field checks of instruments for Quality Assurance purposes were performed in Portland by NEA, in Seattle by DOE staff, and in Spokane by SCAPCA and DOE personnel. Standard operating procedures were developed and provided to field technicians. Filters for all instruments were preweighed by NEA, logged and distributed to field technicians in all three sites. Glass fiber filters were maintained in cold storage from soon after retrieval until final weighing and analysis. Following sampling, used filters were logged in and weighed by NEA staff to determine sample mass, then converted to standard units. Corrections for fine particle deposition on the coarse mode filter were made to gravimetric and elemental data.

2.2 Analytical Protocol

The analytical program consisted of gravimetric analysis of aerosol mass, elemental analysis by x-ray fluorescence, organic/elemental carbon by thermal combustion, Polynuclear Aromatic Hydrocarbons (PNA) by gas chromatography/mass spectroscopy and Carbon-14 by low level β particle counting. Each of these methods is described below. The sampling and analytical techniques used were designed to provide aerosol chemistry information needed to identify RWC impacts by Chemical Mass Balance and Carbon-14 source apportionment methods discussed in sections 2.4 and 2.5, respectively. Table 2 summarizes the sampling and analytical design used as well as the intended purpose of the data collection.

2.2.1 Gravimetric Analysis

Hi-vol Sierra sampler filters used at sites 1-6 were preweighed, conditioned and final weights determined at NEA, INC. using a Torval balance. Replicate filter weights were routinely conducted on 12% of the filters to verify that weights were maintained with ± 10% relative precision. Dichotomous filters were weighed on a Cahn Model 27 electro balance with replicate weighings of 12% of the filters to also insure that weights were held to within ± 10% relative precision. Filter handling, logging, shipping and calculations were conducted in accordance with NEA standard operating procedures. Because of the potential loss of volatile organic hydrocarbons, all hi-vol and Sierra samples were shipped and stored under refrigeration.

Table 2

Program Analytical Design

Sampling Equipment	Sample Provided	Analytical Method*	Provides Data Input to CMB[4]	Carbon-14	PNA[5]	NAAQS
Sierra 235 Impactor	Fine Fraction - Glass Substrate	Combustion[1]	x	x	x	
Dichotomous Impactor	Fine Fraction - Teflon Substrate	XRF, NAA[6]	x			
Hi-vol Sampler	TSP Fraction - Glass Fiber	C-14[2] GC/MS			x	x
Size Selective Inlet	IP Fraction - Glass Fiber	GC/MS[3] C-14		x	x	

* Gravimetric analysis completed on all samples
[1] Combustion oxidation for Elemental/Organic carbon
[2] Carbon-14
[3] PNA compounds by Gas Chromatography-Mass spectrometry
[4] Chemical Mass Balance
[5] Polynuclear Aromatic Hydrocarbons
[6] X-ray Fluorescence/Neutron Activation Analysis

2.2.2 X-ray Fluorescence (XRF)

Fine particle samples collected on dichotomous filters were analyzed for trace elements using x-ray fluorescence (XRF). The technique is based on the fact that atoms within the sample are excited from their ground state to higher energy levels by x-radiation from an x-ray tube. The excited atoms emit discrete energy x-rays as they return to their normal energy level. The energy of the emitted x-rays is characteristic of the emitting element and is used to qualitatively identify the element while the number of x-rays detected is proportional to the number of atoms present and provides a quantitative measure of a specific element's concentration through a direct comparison with standards. Thirty-three elements are commonly measured by this technique, provided their minimum detectable concentrations are greater than those noted in Table 3. Intermethod comparison of XRF and neutron activation analysis for about 7 elements is conducted routinely. A detailed description of potential interferences, calibration calculations and quality assurance procedures is documented in NEA standard operating procedures (Appendix 6).

2.2.3 Neutron Activation Analysis (NAA)

NAA is used (a) to measure the concentration of several elements (Na, Mg) for which quantitative measurements cannot be obtained by XRF analysis and (b) to provide intermethod quality assurance comparisons for 7 other elements measured by both XRF and NAA. The technique requires that the sample be placed in a neutron flux from a nuclear reactor. Elements within the specimen absorb neutrons and undergo nuclear transmutations forming radioactive elements which, in turn, emit radiations characteristic of the specific radionuclides. Since the number of these radioactive elements formed are proportional to the number of original stable element atoms present, measurement of the number of specific radionuclides radiation is an indirect quantitative measure of the stable element concentrations. Counting was done with 30% and 17% ORTEC HpGe gamma-ray spectrometers.

Table 3

X-RAY FLUORESCENCE
MINIMUM DETECTABLE CONCENTRATIONS*
(ng/cm^2)
STANDARD ANALYSES+

Element	
Al	10
Si	8
P	10
S	30
Cl	20
K	6
Ca	6
Ti	2
V	1
Cr	1
Mn	1
Fe	2
Ni	1
Cu	1
Zn	1
Ga	1
As	1
Se	1
Br	2
Rb	4
Sr	4
Y	8
Zr	30
Pd	8
Ag	12
Cd	14
In	15
Sn	15
Sb	15
Ba	100
La	100
Hg	4
Pb	5

* Three sigma interference-free MDC for particulates deposited on filters with 1 mg/cm^2 densities such as Nuclepore and some cellulose and teflon filters MDC $\propto$ $(time)^{-\frac{1}{2}}$ $(filter\ density)^{\frac{1}{2}}$

** For stretched teflon filters

\+ Custom analysis for specific elements at special MDC's available upon request.

2.2.4 Carbon Analysis

Organic and elemental carbon (OC/EC) analysis of a sample aliquot is conducted by heating samples collected on glass or quartz fiber in an oxygen-free atmosphere at a temperature of 600°C to oxidize organic carbon to CO_2 which, in turn, is reduced to CH_4 in a MnO_2 bed heated to 900°C. The methane is then measured by a flame ionization detector (FID). Elemental carbon is then measured by introducing O_2 into the sample oven and combusting remaining carbon to CO_2 which is also reduced to methane and measured by FID. Artifact EC formed from pyrolysis of OC is detected (and corrections made) through the use of an optical filter reflectivity system.

2.2.5 PNA Analysis

Selected Sierra and hi-vol filters were submitted for PNA analysis by gas chromatography/mass spectroscopy. Each sample was extracted for 8 hours with dichloromethane followed by removal of polar compounds on an alumina column and solvent evaporation. Internal standards were added to each sample prior to GC/MS performed as outlined elsewhere.[3]

2.2.6 Carbon-14 Analysis

Sample analysis for Carbon-14 consists of mounting the particle filter directly on the inner wall of a combustion tube and converting the sample carbon to high purity CO_2 by combustion in an oxygen stream over CuO and Ag-wool at 800°C and 400°C, respectively. Final purification of the sample CO_2 is accomplished at low temperature (-78°C) distillation and exposure to Cu-foil at 800°C. Sample mass is then determined by standard gas volumetric techniques.

The ^{14}C content is determined by directly counting the CO_2 at 1-4 atm in a miniature low-level gas proportional counter using massive shielding, meson cancellation and pure counter construction materials. The ^{14}C decay rate is based on β^- particle counting.

2.3 Quality Assurance

The project quality assurance program consisted of four elements each of which are briefly described below:

2.3.1 Ambient Monitor Siting

Each of the ambient monitor sites selected for this study was reviewed with respect to EPA siting criteria described in 40 CFR 58. Each of the sites is described in Appendix 1.

2.3.2 Analytical Program

A brief description of quality assurance elements associated with the analytical program are described in section 2.2 and in greater detail in Appendix 6. Since elemental analysis is central to the CMB source apportionment method, the XRF elemental analysis quality assurance plan is briefly discussed below.

The XRF QA program includes all aspects of the ambient sampling and filter handling protocols. Special precautions were taken in the field and in the laboratory to avoid sample contamination, loss of particles during filter shipment and potential for filter identification problems. Clean room techniques, for example, were used during loading (and unloading) filters from their holders and specially designed sample shipment containers were used to minimize the potential for particle losses due to sample tipping. During XRF analysis, quality control standards and blank samples were analyzed for each group of 10 samples analyzed and results were compared to known standard values to maintain precision to within ± 2%. Sample groups outside of this range were reanalyzed. Analytical results for several elements (K, Ca, Fe, As, Br and Pb) were intercompared between excitation conditions and calibration standards have been verified by extensive interlaboratory and intermethod analysis.

Similar procedures have been followed with respect to organic and elemental carbon analysis results to insure that analytical precision and accuracy is held to within ± 15% relative to the sample concentration. Both internal quality control (replicate analysis of a "standard" filter) and external standards (filters containing known amounts of carbon) were routinely analyzed.

Gravimetric analysis of the ambient samples included replicate analysis (12% audit level) of the filters to maintain weighing precision and consistency of tare and balance calibration checks during each weighing set to sithin ± 0.004 mg of true value.

2.3.3 Field Monitoring Program

Standard operating procedures were developed for Hi-vol and dichotomous sampler calibration, maintenance, filter handling and flow audits to insure consistency within the data set. Each procedure is described in Appendix 6. In addition, notes were maintained to reflect meteorological circumstances in the near vicinity of the sampling site. These notes are included in Appendix 3.

2.3.4 Data Management

Two levels of data validation QA were maintained; (a) verification of the transcribed data against the source documents and (b) examination and resolution, where possible, of inconsistencies in the data sets. For example, bivariate plots of elemental measurements (Pb/Br, Al/Si, etc) were made prior to CMB analysis of the data to identify and validate outliers.

2.4 Sample Selection

Samples submitted for chemical analysis were selected on the basis of (a) fine fraction (< 2.5 μm) mass loading, (b) light scattering (Bscat) average where available, (c) relative meteorological stability (wind speed and air stagnation advisories) and (d) daily minimum temperatures.

The above criteria were used to estimate the probable relative RWC impacts represented by sample filters. As noted earlier, filters likely to reflect maximum impacts were selected. Other criteria which influenced selection and ranking of filters recommended for analysis included:

1. Completeness of data for best CMB analysis
   Ideally, respirable particulate samples for both inorganic and carbon analysis are desirable at both the urban monitoring site, and a suitable background site during the same 24 hour sampling period. However, this ideal situation devotes considerable resources to analysis of background samples, and was often not possible, due to lack of (a) respirable particle size samples, (b) background samples taken on same day (c) pairs of samples suitable for organic and inorganic analysis.
2. Available Background Samples
   Analysis of enough background samples to describe a range of potential background RWC impact on days of expected high RWC impact at urban sites.
3. Preference for Analysis of Respirable Particulate Samples
   RWC emissions are assumed to be almost entirely in the respirable size range (≤ 2.5 microns). Accordingly, preference was given to inorganic analysis of dichotomous sampler fine fraction filters and companion carbon analysis of Sierra filters (< 2 μm). If, however, a SSI sample (< 15 μm) was used for carbon analysis, companion elemental analysis was completed on both dichotomous fine and coarse filters and summed together to obtain comparable sets of data for an inhalable size fraction.
4. Consistency of Mass Loadings on Co-located Samplers
   In some cases, (Boise) samples with possible high RWC impacts were not selected for analysis because of apparent discrepancies in mass loadings on filters from co-located samplers, e.g., (a) too large a difference in dichotomous fine + coarse mass and hi-vol (SSI) mass, or; (b) standard hi-vol TSP mass loadings significantly lower than respirable or inhalable samples taken during the same 24 hour period at the same site.
5. Availability of Recommended Filters for Analysis
   Availability of both the urban and background samples for analysis was a prerequisite to sample selection.

The process of selecting filters for analysis was proceeded by first assembling available data on the mass loadings of respirable, inhalable and total suspended particulate (TSP) samples collected during the October, 1980-March, 1981 period. Since dichotomous samplers were operating in a number of

cities in Oregon, Washington and Idaho, it was feasible to concentrate on respirable particle size samples in the following cities:

Oregon	Washington	Idaho
Portland	Seattle	Boise
Eugene	Spokane	
Medford	Yakima	
Bend	Longview	

Lack of dichotomous samplers, and other considerations, ruled out selection of filters from some cities of potential interest (i.e., Olympia, Washington). Second, samples associated with higher 24 hour average Bscat values were assumed to correspond to higher RWC impacts. Peak Bscat values which occurred in the evening and early morning hours also were assumed to indicate potential RWC activity. The third consideration involved selecting samples associated with maximum atmospheric stability and cold weather, as represented by low surface wind speeds and low daily minimum temperatures, respectively. The fourth and primary criteria for selection were the fine particle mass concentrations.

Eighteen Sierra and SSI samples from five Northwest cities were selected for PAN analysis to (a) indicate potential human exposure to hazardous chemicals and (b) to determine if PAN concentrations were correlated with RWC impacts determined by CMB and Carbon-14 analysis. In addition, 13 samples were selected for Carbon-14 analysis to provide a second, independent estimate of RWC impact. Both sets of samples were selected in accordance with the criteria described above.

3.0 SOURCE APPORTIONMENT

Identification of RWC particulate impacts requires the application of methods capable of apportioning aerosol mass among possible sources. Chemical receptor models have been selected for use in this study because these methods do not rely on emission inventory or meteorological data as a basis for

quantification of source impacts. Two independent, yet complementary receptor model approaches have been included in this program design. Each are discussed in the following sections.

3.1 Chemical Mass Balance

The chemical mass balance model matches source particle size and chemical "fingerprints" to those measured at the receptor to back-calculate the impact of specific source classes of similar chemical composition. Given data on ambient concentrations of several chemical species and the percent by weight of those species in the source emissions, a set of equations is prepared and solved to determine source impacts.

3.1.1 Chemical Mass Balance Receptor Model

The starting point for the Chemical mass balance model is essentially the same as the source (dispersion) model. The source model states that the contribution of a source to a receptor is dependent upon the emission rate and a dispersion factor. Limitations of dispersion modeling, however, arise from difficulty in quantifying dispersion factors in areas of complex terrain and/or meteorology, from difficulties in identifying emission rates, and other operating parameters associated with emission sources. The advantage of the CMB, and other receptor approaches, is that an exact knowledge of these parameters is unnecessary.

The basic assumptions inherent in the CMB approach are the same as those associated with other receptor and source (dispersion) models:

The particulate mass measured at the receptor is a direct, linear sum of the mass contribution from a number of specific sources

$$m = \sum_{j=1}^{p} M_j \qquad (1)$$

where

m = measured concentrations of particles from all "p" sources ($\mu g/m^3$)

M_j = the impact at the receptor of source "j" ($\mu g/m^3$)

Similarly, the concentration of a given chemical species is assumed to be the sum of the contributions from each individual source emitting that species.

$$C'_i = \sum_{j=1}^{p} F_{ij}' X_{ij} M_j \qquad (2)$$

where

C'_i = measured concentration of species "i" from all sources "p" ($\mu g/m^3$)

F_{ij} = the fraction of species "i" in the emissions of source "j" as measured at the source

X_{ij} = the coefficient of fractionation of species "i" in the emissions of source "j". Fractionation is a systematic change in relative species abundances as the aerosol ages due, for example, to gravitational settling or condensation of volatile organic hydrocarbons

M_j = the impact at the receptor of source "j" ($\mu g/m^3$)

The F_{ij}' values associated with major emission sources are measured or adapted from literature values, and the C_i data are obtained through field monitoring programs. One can ensure a fractionation coefficient which approaches unity by (a) using stack gas dilution techniques to ensure capture of condensible aerosols and (b) obtaining size-resolved source composition and ambient aerosol measurements. By conducting fine and coarse mode CMB calculations, source composition (F_{ij}') errors due to gravitational settling of large particles can be minimized. If no further fractionation or source emission composition changes are assumed to occur, then X_{ij} is assigned a value of unity and F_{ij}' can be considered to remain unchanged in time and distance downwind when measured at the receptor ($F_{ij}' = F_{ij}$).

By dividing both sides of equation (2) by the particulate mass collected at the receptor, all of the variables in the equation are expressed as a ratio to the aerosol mass:

$$C_i = \sum_{j=1}^{p} F_{ij} S_j \quad (i=1 \text{ to } n) \qquad (3)$$

where

C_i = concentration of species "i" expressed as a ratio to mass (i.e., $C_i = C'_i / \sum_{j=1}^{p} M_j$)

F_{ij} = the fraction of species "i" in the emissions from source "j" at the receptor, expressed as ratio to mass

S_j = the impact at the receptor of source "j" expressed as a ratio to mass emitted from all sources impacting the receptor(i.e., $S_j = M_j / \sum_{j=1}^{p} M_j$)

n = the number of chemical species considered

p = the number of sources impacting the receptor.

Since S_j is the quantity to be determined, a set of simultaneous equations can be written for all "p" sources of species "i", where "i" is defined as a "fitting" element. Once the set of equations are formed, the value of S_j can be solved by standard matrix manipulation techniques using linear least squares or effective variance solutions utilizing commonly available matrix mathematics.

The effective variance least squares fitting method used by NEA, INC. in this study weights the solution in accordance with uncertainties in both the source composition (F_{ij}) and the ambient aerosol species (C_i). The procedure ensures that those components with the greatest uncertainty receive less weight in the fit and that both sources of uncertainty are propagated through to the source impact (S_j) determination.[2]

Uncertainties in the source impact estimates are calculated by an error propagation algorithm incorporating (a) the imprecision in the ambient aerosol chemical species (C_i) analysis and (b) the variability in the source composition species (F_{ij}) at the one sigma level.

3.1.2 Source Characterization

The data sets referred to below and included in the Appendix have been developed by comprehensive analysis of representative source test samples, or adapted from the literature cited. In all cases, source emissions have been collected using size segregated (fine, coarse) sampling systems. Hogged fuel boiler and residential wood combustion samples were taken with a size segregating source testing procedure for aerosols. Following sample collection, the filters were analyzed for organic and elemental carbon content, ions (SO_4^{-2}, NO_3^-, Cl^-, F^-) and trace metals. Source emissions are then characterized in terms of weight percent. Further detail on the sampling protocol may be found in the references cited. The source signature described in this section forms an essential element of the CMB source apportionment analysis. References to the origin of the emission chemistry used are noted below.

Mneumonic	Source	Emission Chemistry Origin	Reference
RDUST	Geologic	Local soil samples were collected in the vicinity of the Boise site (5 samples), Spokane-Country Homes (3 samples) and Seattle-Newport Way (4 sites). Following laboratory processing, resuspension and preliminary XRF analysis, composite soil chemistries were formed for comprehensive XRF analysis. City specific soil chemistry was then used in association with samples from each community. Although the mneumonic RDUST is used in the CMB calculations, the soil chemistry used cannot distinguish between native soils, paved road dust, unpaved road dust or other sources of similar aerosol chemistry.	-
RESWD	Residential Wood Combustion	Medford Aerosol Characterization Study	4
TRANS	Transportation	Medford Aerosol Characterization Study	4
HOGFU	Hog Fuel Boiler	Medford Aerosol Characterization Study	4
ALUMR	Aluminum Reduction	Portland Aerosol Characterization Study	5
RDOIL	Residual Oil Combustion	Portland Aerosol Characterization Study	5
SECSO	Secondary Sulfate	Based on excess sulfur calculated as sulfate Portland Aerosol Characterization Study	5
GALVN	Galvanizing operations (or other zinc rich source)	Based on excess zinc	
MARIN	Marine Aerosol	Portland Aerosol Characterization Study	5
CDUST	Continental Dust	Portland Aerosol Characterization Study	5
KRAFT	Kraft Recovery Furnace	Portland Aerosol Characterization Study	5

3.2 Carbon-14

Measurements of radioisotope carbon-14/carbon-12 ratios have been used by Cooper and Curie to distinguish between "modern" and fossil fuel-derived carbonaceous aerosol, providing an important new method of RWC impact assessment. The method's ability to resolve these two classes of sources is based on the fact that the isotopic ratio of $^{14}C/^{12}C$ in plant and animal tissue is in equilibrium with the same ratio in atmospheric CO_2, whereas fossil carbon contains essentially no radiocarbon (^{14}C) because of its old age compared to the half life of the ^{14}C isotope (5730 years). Consequently, carbon 14 is a unique tracer of carbonaceous aerosol from contemporary carbon sources (such as wood combustion) and can be used to apportion the carbon content of the aerosol.

Application to RWC impact analysis requires knowledge of (a) $^{14}C/^{12}C$ ratio in the fuel being burned, (b) contemporary carbon source activities impacting the receptor (i.e., structural fires, forest fires, open burning of residential debris, incineration) and (c) the carbon content of RWC emissions. Samples submitted for analysis must be size fractionated to minimize interference from large particle contemporary carbon sources, such as leaf fragments. Each of the three requirements are addressed below:

3.2.1 Fuel Ratio Measurements

Interpretation of ambient carbon $^{14}C/^{12}C$ ratios requires a knowledge of the isotope ratio in the fuel burned in the community. If the ratio is significantly greater than 100%, corrections in the assumptions are required. Four samples of typical wood fuel burned in Northwest communities were analyzed by the $^{14}C/^{12}C$ method. Fuel samples were formed following completion of a telephone survey of wood suppliers, U.S. Forest Service and university extension agents in Boise, Seattle, Portland and Spokane. Representative logs of each of the species were obtained from each city and composite source samples formed based on their relative use shown in Table 4. Cuts were made perpendicular to the concentric growth rings to insure that sawdust samples were integrated in correct proportion to the age of the "fixed" carbon contained in the logs.

Table 4

Relative Wood Type Use
Data Used to Form ^{14}C Fuel Samples

City	Species	Percent in Composite Sample
Seattle	Alder	70%
	Douglas Fir	30%
Portland	Alder	20%
	Douglas Fir	60%
	Hemlock	20%
Spokane	Douglas Fir	30%
	Western Larch	40%
	Ponderosa Pine	15%
	Lodge Pole Pine	15%
Boise	Douglas Fir	40%
	Ponderosa Pine	30%
	Lodge Pole Pine	30%

The results of the ^{14}C analysis of these samples are listed below in terms of percent of modern carbon and are in very close agreement to previously published values (109%) measured relative to international radiocarbon standard.[2] The Seattle result (133 ± 2%) is substantially greater than the mean of the other three samples (111 ± 4.6). No explanation for this discrepancy was found.

Table 5

Carbon-14 Analysis Results
For Typical Wood Fuels

Airshed	% Modern Carbon
Portland	115 ± 1*
Boise	106 ± 1
Spokane	112 ± 1
Seattle	133 ± 2
Mean	116.5 ± 11.6%

* Analytical errors exclusive of sampling uncertainty

As noted in section 1.0, the objective of this program was to quantify the maximum 24 hour impact of RWC emissions in Pacific Northwest communities during the 1980-81 heating season. Results presented in this document, however, largely represent air quality impacts measured during the month of February, 1981--a period during which the average heating load demand was less than that which typically occurs during the period of peak residential space heating demand (November, December and January). Data reported herein therefore represents high impact days selected from samples collected during a period of moderate weather conditions. Higher impacts may occur during periods of greater space heating demand and poorer atmospheric dispersion.

Program results for Medford, Seattle (South Park and Georgetown), Spokane (County Health) and other sites where 4 or less samples were analyzed, cannot provide a comprehensive understanding of the actual magnitude of RWC emission impacts at these sites. Instead, results for these communities should be viewed as preliminary estimates of likely worst case impacts representative of the sampling period.

Table 6 summarizes, by site, CMB estimates of RWC air quality impacts measured (a) during the field monitoring program and (b) from selected historical samples. Figure 1 illustrates average source contributions to the fine particle mass in Spokane, Seattle and Portland, as well as inhalable mass fraction in Boise. Table 7 includes results of Polynuclear Aromatic Hydrocarbon (PNA) analysis for selected samples from five Northwest cities, and Table 8 lists average TSP, fine mass and RWC impacts for concurrent samples (only) by site. Results of the carbon-14 analysis are presented in Table 9 and Figure 2.

5.0 DISCUSSION OF RESULTS

The Chemical Mass Balance results reported herein are often associated with relatively high levels of uncertainty based on (a) imprecision in analytical measurement of ambient samples and (b) uncertainty in the RWC emission chemistry reported in Appendix 2. Since the RWC source composition values in this analysis were developed during the Medford Aerosol Characterization Study, the impact estimates reported assume a fireplace/wood stove ratio similar to Medford (0.63).

Table 6

CMB Estimates of RWC Impacts
(October, 1980-March, 1981)
Fine Particle Fraction
($\mu g/m^3$)

City	Site No.	No. of Samples	Site Name[3]	Average RWC Percent of Fine Mass	Average Fine Mass	Average Impact	24 Hour Maximum	24 Hour Minimum	Average RWC Background	Locally Generated RWC Impact
Washington										
Spokane	1	15	Country Homes (R)	81.0	55.0	44.5 ± 11.5	68.1 ± 16.0	19.9 ± 12.6	6.8 ± 3.4	37.7
Spokane[A]	13	1	County Health (C)	64.7	53.1	34.3 ± 21.3	-	-	6.8 ± 3.4	27.5
Spokane[A]	14	4	Crown Zellerbach (I)	45.3	37.0	16.7 ± 14.9	19.1 ± 17.3	14.9 ± 12.3	6.8 ± 3.4	9.9
Seattle	3	10	Newport Way (R)	83.8	36.1	30.2 ± 8.6	48.8 ± 13.8	8.2 ± 2.6	9.4 ± 2.8	20.8
Seattle[A]	8	2	South Park (R)	65.8	-	-	68.2 ± 19.9	65.9 ± 19.6	9.4 ± 2.8	57.7
Seattle[A]	10	3	Georgetown (I)	73.4	39.7	29.1 ± 20.2	35.5 ± 24.3	20.4 ± 15.3	9.4 ± 2.8	19.7
Tacoma	9	4	Fire Station #12 (I)	74.9	47.0	35.2 ± 25.8	44.3 ± 32.2	20.3 ± 14.6	-	
Yakima[A]	11	4	Courthouse (C)	93.1	53.8	50.0 ± 34.9	55.1 ± 32.4	48.0 ± 37.7	-	-
Longview[A]	12	4	City Shops (C)	61.4	41.8	25.6 ± 17.8	40.5 ± 24.1	14.2 ± 9.2	-	-
Idaho										
Boise[A]	15	9	Fairview & Liberty St. (C)	69.5	121.8	84.7 ± 42.3[1]	127.9 ± 29.9[1,4]	50.0 ± 13.4[1]	-	
Oregon										
Portland	5	8	Whitman School(R)	68.5	40.0	27.4 ± 10.3	49.0 ± 13.6	13.7 ± 3.9	7.4 ± 5.2	20.0
Medford[A]	7	1	Courthouse (R)	-		-	62.2 ± 19.0		-	

Notes:

[1] Inhalable Fraction (≤ 15 μm) - upper limit RWC impact estimates

[2] 8 hour sample.

[3] Site key
- R - Residential
- C - Commercial
- I - Industrial

[A] Historical Samples

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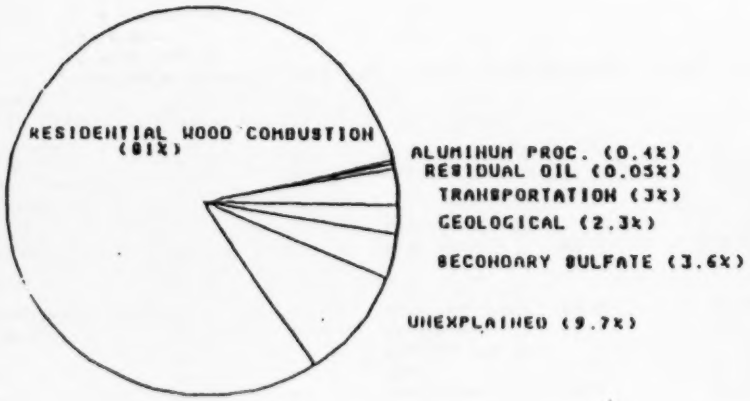
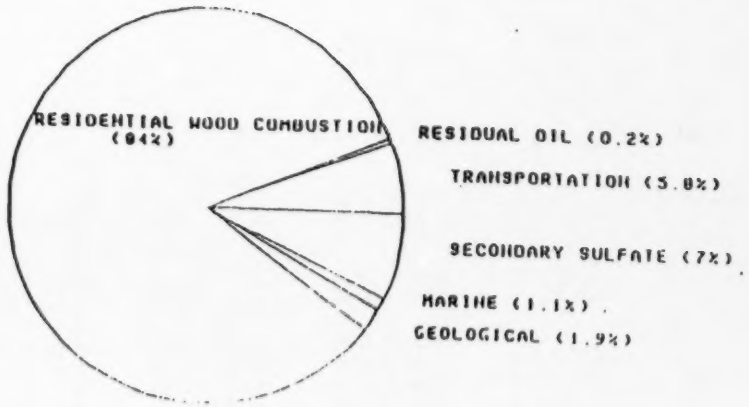
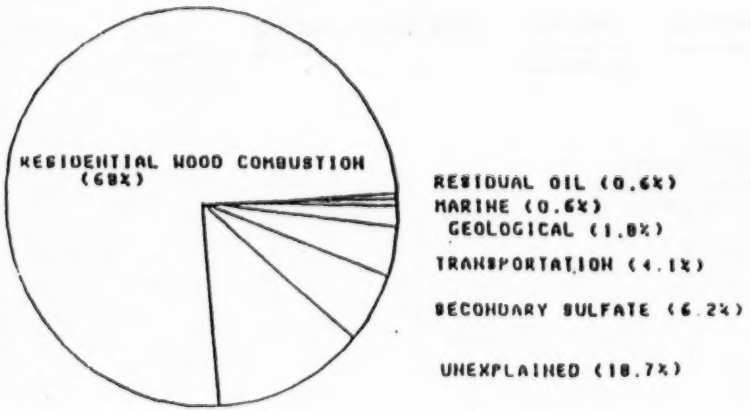
Figure 1
Average 24 Hour Worst Case
Source Contributions
-Fine Particle Fraction-
(October, 1980-March, 1981)



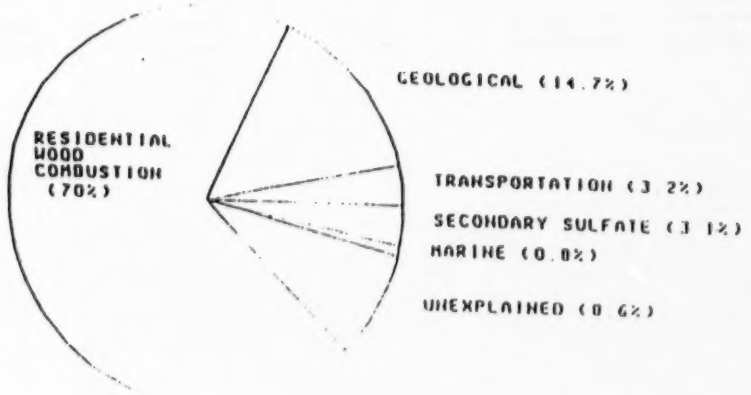
SPOKANE COUNTRY HOMES SITE 1



SEATTLE NEWPORT WAY SITE 3
(Bellevue)



PORTLAND MARCUS WHITMAN



BOISE FAIRVIEW & FIRESTONE etc

Table 7

PNA Analysis Results
For Selected RWC Samples
(ng/m^3)

City	Site†	Date	Sampler	benz(a) anthracene	benzo-fluoranthenes	benzo(a) pyrene	fluor-anthene	pyrene	dibenz-anthracenes	benzo(ghi) perylene
Seattle[1]	Newport Way (R)	2/6	S*	8.9	3.0	1.8	1.9	2.9	--	0.9
Seattle[1]	Newport Way (R)	2/7	S	5.2	9.6	4.2	3.0	5.3	0.7	3.3
Seattle[1]	Newport Way (R)	2/8	S	0.6	0.3	0.3	0.5	1.0	--	0.2
Seattle	South Park (R)	1/15	Hi Vol	48.2	13.6	6.5	11.9	16.2	0.9	7.1
Seattle	South Park (R)	1/16	Hi Vol	7.8	1.8	1.0	3.2	4.7	--	1.2
Seattle[1]	Lake Samamish (B)	3/9	S	--	0.8	0.3	0.1	0.1	--	0.3
Spokane	Country Home (R)	2/1	S	38.6	18.1	11.1	42.2	69.9	1.0	4.5
Spokane	Country Home (R)	2/6	S	50.7	6.0	3.6	39.0	45.0	0.2	1.8
Spokane	Country Home (R)	3/1	S	8.6	13.2	3.7	5.4	9.3	1.4	6.6
Spokane	Turnbull (B)	2/6	S	0.1	0.3	--	0.3	0.4	--	--
Portland	Marcus Whitman Sch (R)	1/31	S	13.6	3.2	1.5	2.8	3.5	--	1.3
Portland	Marcus Whitman Sch (R)	2/7	S	43.9	11.6	5.4	23.6	27.9	0.2	2.9
Portland	Marcus Whitman Sch (R)	3/5	S	14.3	5.4	2.7	2.9	3.9	--	2.1
Portland	Carus (B)	2/6	S	0.4	1.5	0.5	0.4	0.6	--	0.7
Boise	Fairview & Liberty (C)	1/8	SSI**	1.3	3.6	2.3	0.7	0.8	--	1.5
Boise	Fairview & Liberty (C)	12/12	SSI	0.9	1.6	0.8	0.3	0.3	--	2.3
Medford	Courthouse (C)	12/17	S	27.6	12.4	8.5	12.4	15.9	--	3.4
Medford	Courthouse (C)	1/16	S	22.5	8.3	8.3	10.4	9.0	--	3.1

* Sierra Model 235 Impactor
** Size Selective Inlet

Minimum Detectible Concentrations:

fluoranthene, pyrene, benz(a)anthracene, benzofluoranthenes, benzo(a)pyrene) 0.05 ng/m^3

benzo(ghi)perylene, dibenzanthracene) 0.1 ng/m^3

† Site key
(B) Background (C) Commercial
(R) Residential (I) Industrial

1 Located in Bellevue, Washington

Table 8

TSP, Fine Particle and RWC
Impact Averages
(Concurrent Samples, Only)

City/Site*	No. of Obs.	TSP Mass Mean ± Std. Dev. ($\mu g/m^3$)	Fine Mass Mean ± Std. Dev. ($\mu g/m^3$)	RWC Impact Mean ± Std. Dev. ($\mu g/m^3$)	RWC Impact % of TSP Mass
Spokane					
Country Home (R)	13	118.9 ± 50.9	53.0 ± 17.7	44.8 ± 14.9	36.5
Crown Zellerbach (I)	3	232.0 ± 156.9	16.4 ± 0.5	37.6 ± 2.4	11.1
Seattle					
Newport Way (R)	9	71.7 ± 22.8	33.8 ± 10.5	29.4 ± 11.0	42.0
Tacoma					
Fire Station 12 (I)	4	159.0 ± 56.7	47.0 ± 5.5	35.2 ± 9.7	29.7
Portland					
Whitman School (R)	8	62.1 ± 19.7	43.3 ± 15.1	27.3 ± 10.3	43.9
Yakima					
Courthouse (C)	3	221.6 ± 87.1	55.3 ± 12.4	50.6 ± 4.0	25.6
Boise					
Fairview & Liberty (C)	9	148.7 ± 59.3	121.6 ± 43.5**	84.6 ± 26.9**	60.4

* Other city sites have less than 3 concurrent observations
** Inhalable particulate mass (< 15μm)
C = Commerical I = Industrial R = Residential

Table 9

Comparison of RWC Impact Estimates
Based on CMB and Radiocarbon Measurements

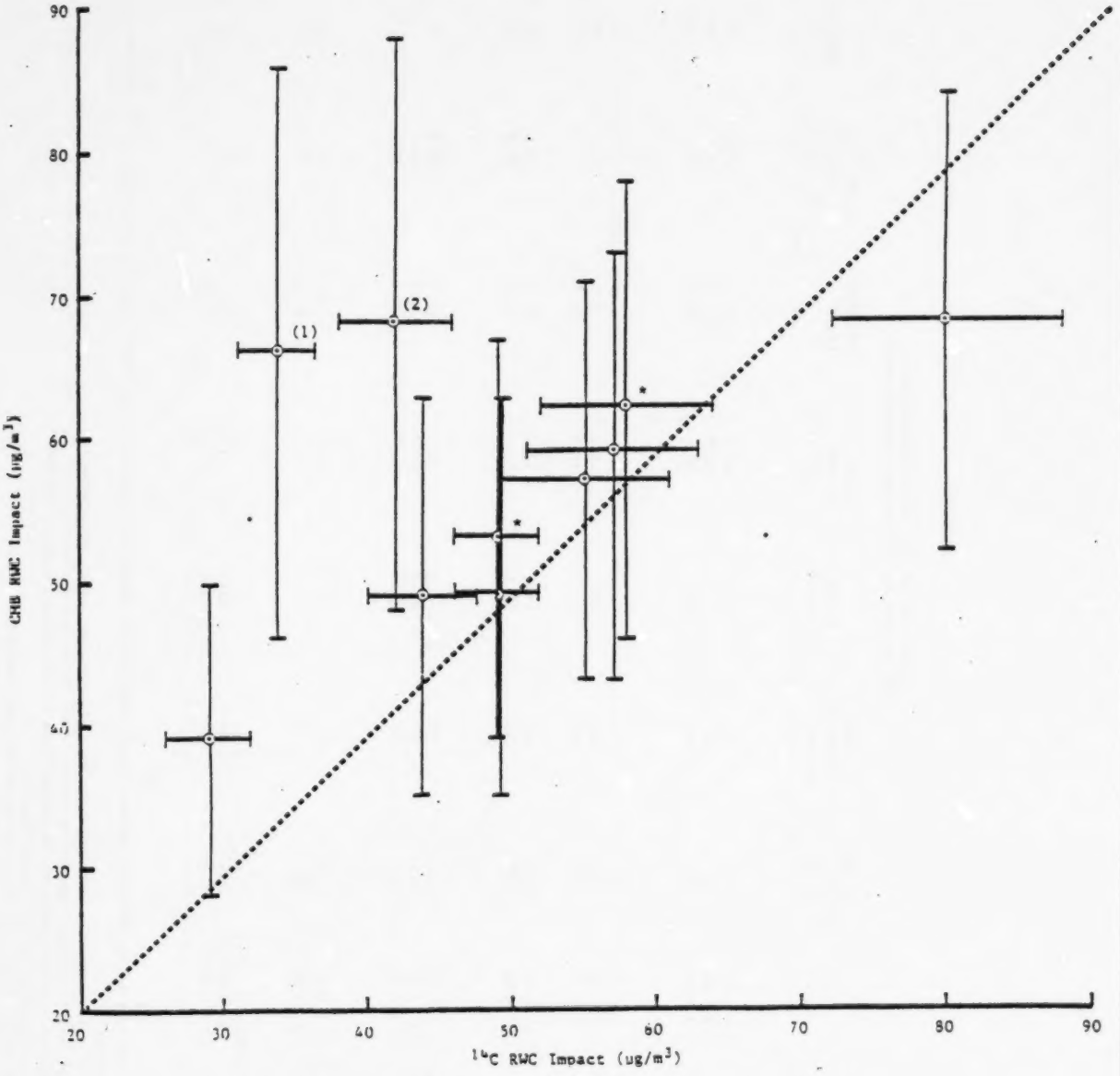
City/Site	Date	% Modern Carbon in Wood (B)	% Modern Carbon in Aerosol (A)	% RWC (C=A/B)	Total Carbon ($\mu g/m^3$)(D)	RWC Carbon ($\mu g/m^3$) (E = D ÷ C)	RWC ^{14}C ($\mu g/m^3$) (F = E/0.6)	CMB Estimate $\mu g/m^3$	^{14}C/CMB Ratio
Spokane									
Country Homes	3-1-81	112	97	86.6	40.1	34.7	57.9	59 ± 16	0.99
	2-6-81	112	107	95.5	34.8	33.2	55.4	57 ± 14	0.96
	2-1-81	112	118	(100)	48.3	48.4	80.5	68 ± 16	1.18
Seattle									
Newport Way	2-6-81	133	----------	----------	----------	sample lost	----------	----------	----------
	2-8-81	133	96	72.2	24.2	17.4	29.0	39 ± 11	0.75
	2-7-81	133	100	75.2	35.4	26.7	44.4	49 ± 14	0.91
South Park	1-16-81	133	63	47.4	53.7	25.5	42.4	68 ± 20	0.62
	1-15-81	133	53	39.8	52.4	20.9	34.8	66 ± 20	0.53
Portland									
Harcus Whitman	3-5-81	115	96	83.5	32.5	27.1	45.2	49 ± 14	0.92
	1-31-81	115	97	84.3	35.9	29.3	48.9	(53)[G]	0.92
	2-7-81	115	90	78.3	44.9	35.1	58.6	(62)[G]	0.95
Boise									
Fairview & Liberty	1-8-81	106	64	60.4	54.5	32.9	54.9	79 ± 21	0.69
	12-12-80	106	24	22.6	94.1	21.3	35.4	123 ± 33	0.29
Medford									
County Court-house	12-17-80	111	104	93.7	45.8	42.9	71.5	53 ± 19	1.35
	1-16-81	111	114	(100)	44.1	44.1	73.5	62 ± 19	1.18

Notes

(B) Calculated in relation to international radiocarbon standard. Values are greater than 100% because of ^{14}C generated during nuclear atmospheric testing.
(A) % of modern carbon in atmospheric CO_2, adjusted to age of wood burned.
(C) % of modern carbon from RWC sources. 100% is an upper limit.
(D) Measured total carbon concentration (sum of elemental, organic carbon).
(E) Concentration of TWC carbon ($\mu g/m^3$).
(F) RWC impact based on ^{14}C, corrected for associated H, O, N.
(G) CMB estimates from filters of uncertain total sample volume.

Figure 2

^{14}C Validation of CMB Impact Estimates ($\mu g/m^3$)
(with associated uncertainty error bars)



*CMB estimates from filters of uncertain total volume

(1) Seattle South Park 16 Jan. 1981

(2) Seattle South Park 15 Jan. 1981

Although the fuel use survey (task 2B) results indicate different fireplace/wood stove emission ratios for Portland, Seattle and Spokane (0.45, 1.94 and 1.77, respectively), an insufficient body of source emission chemistry for fireplaces and wood stoves is available to clearly differentiate between these two sources. Apportioning impacts between fireplace and wood stove emissions is further complicated by the high degeee of variability in the composition of the emissions. Given the level of effort that had previously been committed to development of the Medford RWC emission composition data, the difficulties noted above and the presence of independent validation of CMB-derived RWC impacts during the Medford Aerosol Study (based on C-14 results), further attempt to modify the Medford emission chemistry data were not attempted.

RWC impact estimates derived by the CMB methods have been compared to independent measurements made by radiocarbon techniques. Impact estimates obtained from these two methods (Table 9) show relatively good agreement for samples collected at most sites. Discrepancies noted at the Seattle South Park and Boise Fairview and Liberty locations may be caused by a number of factors including (a) deviations from the fuel use mix assumption, (b) the presence of important contemporary carbon sources other than residential wood combustion or (c) errors in the CMB calculations. Each are discussed more fully below.

A. Wood Fuel Mix

Since the ^{14}C estimates are based on an average age (^{14}C content) of firewood in each community, deviations from the wood specie weightings assumed for each city (Table 4) will result in an error in the percent of modern carbon in the ambient aerosol. For example, if residents in the near vicinity of the Seattle South Park site burned a lesser proportion of alder to Douglas fir than estimated on a city-wide basis, the radiocarbon estimates would be higher than estimated. If the mean percent of modern carbon in Seattle fuels is assumed to be nearer to the average value for other Pacific Northwest (116%), RWC estimated by ^{14}C would increase by about 13%.

B. Other Contemporary Carbon Sources

The radiocarbon method quantifies the total amount of contemporary carbon in the ambient aerosol whereas the CMB estimates of RWC impact

are calculated on the basis of numerous aerosol components. An exact match between estimates developed by both methods requires that essentially all of the contemporary carbon measured by the ^{14}C technique be associated with RWC sources--an assumption that may not be valid where (a) the upper size cut of the ambient sampling system allows capture of carbonaceous particles of large aerodynamic diameter (> 2.5 μm) such as plant fibers or (b) industrial sources utilizing wood waste (e.g., Hogged fuel boilers) are major carbon emission sources.

C. Errors in CMB Calculations

Close examination of the CMB calculations for several of the sampling sites indicates the potential for inclusion of distillate oil combustion impacts in the fitting process. Calculations for the South Park site (site 8, Appendix 5) indicates that, by reason of the underestimate of sulfur, distillate oil may be an important component. If so, it would contribute to a 30% overestimation of the RWC impact. The rationale for excluding distillate oil from the CMB fitting process is explained below.

Site average RWC impacts ranged from 16.7 (Spokane-Crown Zellerbach) to 83.7 $\mu g/m^3$ (Boise-Fairview & Liberty St.) and represented from 20% (Medford) to 93% (Yakima) of the fine particle mass. The highest 24 hour impact (128 $\mu g/m^3$) was found at the Boise site. The lowest average impacts (16-30 $\mu g/m^3$) were measured at the background and industrial sites (Tacoma, excepted) while residential sites varied from 30 to 45 $\mu g/m^3$.

RWC impact estimates obtained for Boise are significantly higher than those obtained in other Northwest cities. The maximum impact measured in Boise occurred on January 18, 1981 at the Fairview & Liberty site, 127.9 ± 29.9 $\mu g/m^3$, 8 hour average. These source impact estimates are based on inhalable particulate samples captured on Teflon and glass fiber filters rather than fine particle (< 2.5 μm) samples. As a result, CMB estimated RWC impacts must be considered to be upper limit values subject to considerable uncertainty. The uncertainty is associated with (a) the RWC source composition which is based on measurements of fine particle emissions (b) RWC impact estimates are highly dependent on measurements of K, Cl, elemental and organic carbon, components which in the size fraction greater than 2.5 μm, can become associated with sources other than wood burning emissions.

Discrepancies between SSI and dichotomous sampler mass measurements reported for co-located, concurrent samples further complicates data interpretation. For these reasons, further verification of the Boise results is recommended.

The maximum industrial source impacts, while minimal, were noted at the Longview site (Kraft recovery furnace and aluminum reduction), Tacoma Fire Station 12 (aluminum reduction) and the Spokane-Crown Zellerbach site (Hog fuel boiler and aluminum reduction emissions).

In addition, the chemistry of a large number of samples could be explained by inclusion of a distillate oil source rather than a secondary sulfate source. This would tend to reduce the impact of RWC sources by about 30%. However, since the quality of the CMB fits were (a) quite similar in either case and (b) distillate oil combustion impacts at the background sites were similar to residential sites, distillate oil combustion was not routinely included as a source. It is likely, however, that oil combustion associated with residential space heating is an important contributing source to which a portion of the measured sulfur should be assigned.

The Chemical Mass Balance calculation performed successfully apportioned greater than 90% of the measured mass with reasonable agreement between measured and model-predicted element concentrations. Occasional overpredictions of the mass, however, occur due to uncertainty in the gravimetric analysis or in the source assignments. In most cases, the calculated and measured mass values are within the estimated mass uncertainty.

Analysis of selected samples for PNA compounds was completed because of concern about risks to public health associated with these potentially carcinogenic compounds. Review of RNA analysis results associated with this study suggests that mean concentrations within residential areas are an order of magnitude higher than similar measurements at background sites. Table 10 presents a summary of average PNA concentrations from residential sites during the 1980-81 heating season. Since the samples selected for analysis were intended to reflect worst case RWC impacts, the values reported do not indicate typical conditions.

Table 10

Average PNA Concentration
For Residential Sites (ng/m^3)*
(1980-'81 Heating Season)

PAH Group	Arithmetic Mean	Standard Deviation	Maximum Value	Minimum Value	Arithmetic Mean Background
Benzo(a)Anthracene	19.5	17.3	50.7	0.6	0.2
Benzofluoranthenes	7.4	5.2	18.1	0.3**	0.9
Benzo(a)Pyrene	4.1	3.1	11.1	0.3**	0.4
Fluoranthene	10.6	13.2	42.2	0.3**	0.3
Pyrene	14.4	18.9	69.9	0.3**	0.4
Dibenzanthracenes	0.3	0.4	1.4	0.05	0.05
Benzo(ghi)perylene	2.7	1.9	6.6	0.2	0.3

* Average of 15 selected 24 hour samples
** One-half minimum detectable concentration

PNA measurements made during this study can be compared to annual average measurements of B(a)P during the 1960's in Portland, Eugene and Medford which ranged from 2.3 to 4.8 ng/m^3.[5] Quarterly average maximum values of 8.2 ng/m^3 were recorded in Medford in 1968. Although annual and quarterly average B(a)P concentration data are generally not available after 1970, periodic data from other Northwest locations (i.e., Seattle) suggests that concentrations may have decreased during the 1970-76 period and then increased following 1977.[7,8] Routine PNA concentration measurements are no longer conducted by EPA.

The average B(a)P concentrations noted in Table 10 are similar to the annual and quarterly mean values discussed above, but direct comparison is confounded by differences in averaging times.

There are no published studies available which adequately compare the carcinogenic activity of all ten PNA compounds under similar experimental conditions. Similarly, there is no data available concerning human responses

to individual PNA compounds, since environmental exposures to PNA invariably involve contact with complex and usually undefined PNA mixtures. Therefore, an assessment of the cancer risk related to PNA compounds emitted from RWC sources can only be considered when placed in perspective with other sources of exposure. Conversion, however, of ambient PNA concentrations to inhalation intake requires consideration of the volume of air breathed per day (15 m^3 for a 10 year old child and 23 m^3 for an adult male) and a 24 hour average assumed concentration of B(a)P.[9] If an average daily volume of 19 m^3 and an average B(a)P concentration of 4.1 ng/m^3 is assumed, a daily dosage rate of 0.078 µg/day is obtained. This compares to an estimated total B(a)P intake of 0.16-1.6 µg/day associated with food consumption. As a further comparison, Bridbord[10] estimates that smoking 20 cigarettes per day provides an exposure of 0.4 µg/day of B(a)P, suggesting that the average B(a)P concentration identified in this study is equivalent to dosage received by smoking about 4 cigarettes/day. At the maximum B(a)P concentration measured (11.1 ng/m^3, 24 hour average), the dosage is equivalent to 11 cigarettes/day.

The impact of RWC emissions on total suspended particulate (TSP) air quality was found to range from 11% in industrial areas (Spokane--Crown Zellerbach site) to nearly 44% in residential areas (Portland--Marcus Whitman School). In Boise, the RWC impact, calculated on the basis of the inhalable particulate fraction, may contribute as much as 60% to the TSP mass during worst case RWC impact conditions. Although this data clearly documents the importance of wood combustion emissions to TSP air quality under the conditions of this study, direct inference as to the importance of RWC emissions on TSP air quality standard non-attainment is difficult because (a) the RWC impacts cannot be calculated in terms of an annual geometric mean averaging period and (b) the 24 hour worst case RWC impacts included in this study may not represent the 24 hour worst cast TSP concentrations upon which standard attainment is based.

6.0 CONCLUSIONS

Ambient air quality studies conducted during the 1980-81 space heating season in eight Pacific Northwest communities clearly indicate that residential wood combustion (RWC) emissions, as estimated by validated chemical mass balance analysis, are the most important contributor to the fine particle mass less than 2 um. Since the program design sought to determine maximum RWC impacts, the following conclusions reflect reasonable worst case impact conditions rather than, for example, annual average source impacts representative of each community's airshed.

Key findings of Task 1, then, include the following:

- RWC emissions typically account for 66% to 75% of the fine particle mass, while transportation sources contribute 5%, secondary sulfate, 5.6% and all industrial sources less than 0.5%.
- Background RWC impacts were found to range from 3-12 $\mu g/m^3$, 24 hour average--a factor of ten lower than the urban sites, suggesting that 70-80% of the RWC impact is related to local sources.
- Maximum 24 hour impacts exceeded 60$\mu g/m^3$ at residential sites located in Seattle, Spokane, Portland and Medford. Impacts at industrial sites in Longview, Seattle and Tacoma were significantly lower (15-30 $\mu g/m^3$).
- The highest impacts measured in this study were in Boise, Idaho (128 $\mu g/m^3$, 8 hour average). These measurements must, however, be considered as upper limit estimates requiring further verification.
- PNA concentrations measured at urban sites were a factor of ten higher than that measured at the rural background sites. Although the measured PNA concentrations should be of concern, no direct dose-response relationship are currently available in the literature upon which to base a quantitative assessment of public health risk.

Further interpretation of the results of Task 1 are included in the Task 2A report (Analysis of Air Quality Impacts).

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